PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Method of producing Organo-Silicon Polymers

We, METALLGESELLSCHAFT AKTIENGESELLSCHAFT, of 45, Bockenheimer Anlage, Frankfurt-on-the-Main, Germany, a body corporate organised under the Laws of Germany, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of organo-silicon polymers from organosilanes comprising SiH links and/or Si-Si units.

The term "organosilicon polymers" used herein is intended to denote polymers which consist essentially of Si-O-Si units, but which may contain in addition, Si-Si units and SiH links.

It is known that dimethylsilane $(CH_3)_2SiH_2$ when shaken for hours with a 30% solution of caustic soda yields, with the evolution of hydrogen, a slightly turbid solution from which, after acidification with hydrochloric acid, an oil can be separated. Isobutyl silane has also been subjected to hydrolysis with a mixture of ether, ice and caustic soda solution, whereby on evaporation of the ether, an oil was obtained from the separated ether layer which could be burnt to form silica. These oils are probably already organosilicon polymers.

It has moreover been proposed to hydrolyse hydrolysable silanes with the aid of a water and a water-miscible solvent for example alcohol, dioxane, acetic acid, or acetone, in the absence of caustic alkali, but it has been ascertained that when using organosilanes with SiH links and/or Si-Si units, no hydrolysis occurs under these conditions, since hydrolysis would be easily recognisable through the generation of hydrogen. In addition, although most solvents miscible with water are, in the anhydrous condition, utilisable solvents for alkyl silanes with SiH links, nevertheless separation of the mixture into an aqueous phase and a solvent phase containing the silane, occurs immediately on the addition of water. Alkanols, particularly methyl alcohol, are the only exception.

The speed of the generation of hydrogen in the alkaline decomposition of trialkylsilanes in solutions produced from ethyl alcohol, potassium hydroxide or sodium alcoholates and varying amounts of water, has already been investigated and it has been assumed that silanols can be produced by a process of this type.

It has now been found that organosilicon polymers can be produced from organosilanes containing at least one SiH link and/or Si-Si unit, by treating them with liquid mixtures of alcohol, preferably methanol, water and ammonia, condensing if desired with heating, and removing the alcohol, ammonia and water, preferably by evaporation. If desired, the hydrolysis may be carried out to a predetermined degree prior to the completion of the gas generation and the reaction product may be subjected to an oxidation process. The speed of hydrolysis can be regulated by the temperature and the concentrations of ammonia and water.

The process of the present invention offers substantial advantages over known processes. In contradistinction to the use of caustic soda solution, when using ammonia, no acidification or extraction with ether is necessary, but merely a physical separation, preferably evaporation. The substances separated by evaporation, that is to say ammonia, methanol and water can be condensed and re-used. The result is that the hereindescribed process enables organosilanes having SiH links and/or Si-Si units to be converted into organosilicon polymers very rapidly, simply and without losses of auxiliary substances. The yields are approximately quantitative. Since when employing ammonia no acidification or extraction with ether are necessary, there are no losses through the solubility of silanols or their alkali salts in water or through the sparing solubility in ether of a part of the organo-

silicon polymers formed. Organosilicon polymers absolutely free from acid can be produced.

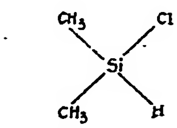
It is entirely unexpected that rapid hydrolysis can be achieved with ammonia; since although for example a 10% solution of caustic soda exhibits intense generation of gas at the surface of contact with diethylsilane at ordinary temperature, nevertheless when using a concentrated aqueous solution of ammonia instead of the caustic soda solution, no generation of gas is observed, but on the contrary such generation of gas occurs only as soon as a drop of methanol is added. The speed of reaction can then be further increased, to the extent in which a caustic soda solution is used, by using an amount of methanol necessary for the dissolution of the entire amount of organosilane.

In the process of the present invention methanol thus acts as dissolving intermediary between alkylsilanes and the water necessary for the hydrolysis and the ammonia, so that in the homogeneous phase a considerable speed of hydrolysis is achieved, even with the weak base, ammonia.

In the hydrolysis according to the present invention, the SiH links or Si-Si units are apparently converted directly into the Si-OH units with the generation of hydrogen, without the formation of alkoxy compounds. It is naturally essential that sufficient water should be present. When using anhydrous alcohol, it is in fact known that the SiH links or Si-Si units pass over into alkoxy units if sodium ethylate is used as catalyst.

The principle underlying the present invention can also serve for the rapid quantitative determination of SiH and Si-Si contents in organosilanes by the determination of hydrogen or weighing out the polysiloxane. Since, in contradistinction to alkylhydrogensilanes, unsubstituted silanes are already rapidly converted into silicic acid by ammoniacal water, gas analysis of gases containing silanes and alkyl silanes can be conveniently carried out.

All organosilanes having SiH links and/or Si-Si units are suitable for use in carrying out the hereindescribed process. The organic radicals may for example be alkyl, chloralkyl and aryl. If in addition to SiH and Si-Si, other hydrolysable groups are also present on the Si, such as for example Cl, OR or OCOR, the hereindescribed hydrolysis can in general be carried out, whereby siloxane bridges, Si-O-Si, may also be produced. If acids are produced by the hydrolysis, it may be necessary to add further ammonia to the reaction mixture, since no hydrolysis of the SiH links and Si-Si units occurs in the acid or neutral medium. If for example,

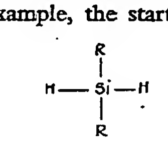


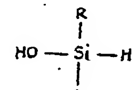
is present, and if it is desired to obtain the largest possible siloxane molecules, it is convenient to complete the hydrolysis and the condensation first in an acid medium on the chlorine atoms and thereupon to carry out the hydrolysis and condensation of the hydrogen atoms in an ammoniacal medium.

Besides methanol, the alkanols used can in principle also be other alcohols, such as for example ethyl alcohol, propyl alcohol, ethylene glycol and glycerine. However, methanol is usually more effective and is moreover more volatile and less expensive, and ethylene glycol and glycerine are for example only poor solvents for the alkyl silanes. In these cases it is convenient to add a further solvent for the organosilanes, for example ether, to the alcoholic solution.

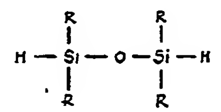
By suitably selecting the starting materials and the reaction conditions, products having accurately predetermined properties can be obtained. For example, by adding inadequate amounts of ammonia or water or by prematurely distilling-off the solvents, products can be obtained which can still generate hydrogen with further amounts of ammonia, i.e. which still have SiH links and/or Si-Si units. These substances are for example hardenable by heating in air, because the SiH links are converted into SiOSi bridges by oxygen. Thus, for example, the viscosity of an organosilicon polymer oil containing SiH links can be increased to a desired degree. Organosilicon polymers which still contain SiH links can also be hardened by simply heating with the exclusion of air, apparently because Si-Si units are formed by the giving-up of hydrogen.

According to one embodiment of the invention the hydrolysing medium, i.e. water and/or ammonia, is added to the alcoholic solution of the organosilanes only slowly whilst thoroughly mixing. Thus, for example, ammonia gas, in certain circumstances also diluted with an inert gas such as nitrogen, can be introduced into the aqueous-alcoholic solution, or water may be added dropwise to the alcoholic solution saturated with ammonia gas. If, for example, the starting material is

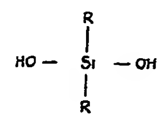
dialkylsilane  monosilanol

 is first mainly produced,

which has time to condense into siloxanes



which then on the further addition of hydrolysing medium are mainly hydrolysed only into monosilanols, so that finally large yields of linear polysiloxanes of high molecular weight are obtained. With rapid hydrolysis the high concentration of hydrolysis media results in very large amounts of silanediols



which can easily condense into cyclic siloxanes of low molecular weight. Accordingly, in the slow hydrolysis of the present invention substances of higher viscosity in the homogeneous phase are produced than in the homogeneous phase with rapid hydrolysis.

For the production of organopolysiloxanes, the starting material as is known, is generally an alkylchlorosilane, which can very easily be hydrolysed. The hydrolysis produces hydrochloric acid. In the process of the present invention, alkylpolysiloxanes can be just as easily produced from the alkyl silanes, which have recently become readily available through the reaction of silanes with, for example, ethylene, in which process hydrochloric acid is neither produced nor needed, so that the products are absolutely free from hydrochloric acid and can be used, for example, for sensitive textiles.

It has been found that the hydrolysis speeds, when carrying out the hydrolysis in accordance with the present invention, are markedly different from one another for compounds of the formulæ R_3SiH, R_2SiH_2, $RSiH_3$ (R being for example C_2H_5), in contradistinction to the corresponding chlorine compounds R_nSiCl_{4-n}, for which the speeds of hydrolysis are approximately equal. In a mixture of different hydrogen silanes any individual silane hydrolyses and condenses largely independently of the others. It thus occurs that in the hydrolysis of the hydrogensilanes, larger siloxane molecules are obtained than in the hydrolysis of the chlorine compounds, in which for example the compound R_3SiCl acts markedly as a chain rupture member in the conversion of R_2SiCl_2 into $(R_2Si\text{-}O)_n$. Since moreover, as is known, a separation of the alkyl silanes is easier, owing to greater boiling point differences, than that of the alkylchlorosilanes, linear organosilicon polymers of high molecular weight and having the known valuable properties can for example be obtained more easily for the same reason.

The process of the present invention which is very simple to carry out, will be illustrated by the following Examples:

EXAMPLE 1

1.28 g. of a fraction boiling at 53 to 57° C. from the reaction of silanes with ethylene at 450° C., and consisting substantially of diethylsilane, were dissolved in 10 cc. of technical methanol, and 8 cc. of concentrated aqueous ammonia solution were added with cooling. A hardly noticeable turbidity occurred temporarily at first, together with intense generation of gas, and an oil layer was at once formed. The mixture can be boiled for a further hour with reflux. No further hydrogen was generated on the addition of caustic soda solution or further ammonia. After distilling off the methanol and water and heating for 24 hours in the drying cabinet, 1.13 g. of polysiloxane oil was obtained. The oil can be used as lubricating oil for hot machine parts.

The products produced by the herein-described process can, as already mentioned, be obtained with widely variable physical properties. They have a wide field of application, for example in the production of damping oils, pump oils, lubricating agents, stopcock grease in the lacquer industry, for electrical and thermal insulation, for heat-resistant packings, corrosion-proof coatings and elastic mouldings.

EXAMPLE 2

2 g. of the light yellow solid reaction product from the reaction of silane i.e. SiH_4 with ethylene at 520° C., composed of $[SiCH_2]_x$, is introduced while stirring into a mixture of propylalcohol and aqueous concentrated ammonia. The mixture is boiled while continuing stirring, under reflux until no further hydrogen is liberated on the addition of potassium hydroxide solution. When prolonging the heating it may be necessary to add further ammonia at intervals. After distilling off the propylalcohol, the ammonia and water, 3 g. of a white silica-like product remains which consists of methylpolysiloxane.

EXAMPLE 3

10 g. of the oily reaction product derived from the reaction of mono- and disilanes with ethylene at 500° C. no longer capable of distilling at normal pressure, and containing as is generally known, different alkylsilanes, having both SiH- and Si-Si bonds, are dissolved in 1.6-hexanediol containing a little water and hydrolysed by the introduction of gaseous ammonia. At normal room temperature the liberation of hydrogen ceases after four hours. After distilling off the 1.6-hexanediol and water 13 g. of a sticky resin-like substance is obtained which hardens on heating in air.

EXAMPLE 4

5 cc. of liquefied monoethylsilane (boiling

point −14° C.), which is obtained by the addition of ethylene to silane at 300° C. and under a pressure of 300 at., is introduced into a mixture of methanol, water and ammonia at minus 80° C. The temperature is then maintained for two hours at −20° C., during which hydrolysis is produced with intensive generation of hydrogen. 5 cc. of an oily layer of ethylpolysiloxane forms on the surface of the methanol and is separated therefrom. Since the hydrolysis is not complete after two hours, this product can be solidified by further oxidation, by adding mercury oxide slowly at normal temperature or faster at slightly increased temperature.

EXAMPLE 5

3 g. dimethylmonochlorsilane $(CH_3)_2SiHCl$ are dissolved in cooled ether and poured into ice-water in a thin stream. After the heat of reaction caused by the hydrolysis of the SiCl-bonds has been dissipated, the hydrochloric acid formed is neutralised by adding ammonia and methanol and the slow addition of ammonia is continued up to the termination of the hydrogen generation due to the hydrolysis of the SiH-bonds. The solvent and ammonia are evaporated and a 3.5 g. of a viscous dimethylpolysiloxane is obtained. This substance can be converted into silicone-rubber by known methods.

What we claim is:—

1). A method of producing organosilicon polymers (as hereinbefore defined) from organosilanes by hydrolysis and condensation, which comprises treating organosilanes containing at least one SiH link and/or Si—Si unit with liquid mixtures of alcohol, preferably methanol, water and ammonia, and condensing the same if desired, by heating.

2). A method as claimed in Claim 1, in which alcohol, ammonia, and water are removed, preferably by evaporation.

3). A method as claimed in Claim 1, in which the hydrolysis is conducted only to a desired degree and the reaction product is subjected to an oxidation process.

4). A method as claimed in any of Claims 1 to 3 in which the ammonia, alcohol and water are removed, preferably by evaporation, before completion of the generation of gas.

5). A method as claimed in any of Claims 1 to 4, in which when using organosilanes with halogen, alkoxy, or other hydrolysable radicals other than SiH links and/or Si—Si units, the hydrolysis of said hydrolysable radicals, and if desired condensation, is or are first carried out in a medium of pH ≤ 7 and thereupon some or all of the SiH links and/or Si—Si units are wholly or partly hydrolysed in an ammoniacal medium.

6). A method as claimed in any of Claims 1 to 5, in which one or more additional solvents for the organosilanes are added to the alcoholic solution.

7). Method of producing organosilicon polymers substantially as described.

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